Supporting Information

Two-step synthesis of fluorescent 3-arylated 1,3a,6a-triazapentalenes *via* a three-component triazolization reaction

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Contents

Experimental procedures and characterization data

Chemicals were purchased from Acros Organics, Sigma Aldrich, Alfa Aesar and TCI Europe and used as received. *p*-Nitrophenyl azide was prepared according to the literature procedure.[1] All reactions were carried out in oven dried glassware, but no special precautions were taken for the exclusion of moisture. Solvents were not dried prior to use. Reactions were carried out under a nitrogen atmosphere unless stated otherwise.

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C. In the case of ambiguous assignments, spectra were run on a Bruker 400 instrument. ^{1}H NMR spectra in $CDCl_3$ were referenced to tetramethylsilane (0.00 ppm) as an internal standard, while ^{1}H NMR spectra in methanol-d_4 were referenced to the methanol-d_4 (3.31 ppm) signal. ^{13}C NMR spectra in $CDCl_3$ were referenced to the $CDCl_3$ (77.16 ppm) signal and ^{13}C NMR spectra in methanol-d_4 were referenced to the methanol-d_4 (49.00 ppm) signal.

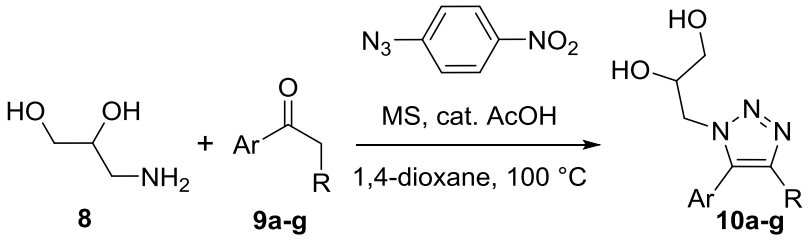
High-resolution mass data were obtained with a Waters Synapt G2 HDMS quadrupole orthogonal acceleration time-of-flight mass spectrometer (ESI mode), for which samples were infused at 3 µL/min and spectra were obtained in positive or negative ionization mode with a resolution of 15000 (fwhm) using leucine enkephalin as lock mass. Low-resolution mass spectra were recorded on a Thermo Finnigan LCQ Advantage instrument (ESI mode). Melting points were taken on a Reichert Thermovar and are uncorrected.

The electronic absorption spectra and absorbances were measured on a Perkin-Elmer Lambda 40 UV–vis spectrophotometer. Corrected steady-state emission spectra were recorded on a Spex Fluorolog instrument. Freshly prepared samples in 1 cm quartz cells were used to perform all UV–vis absorption and fluorescence measurements. These experiments as a function of solvent allowed us to determine the spectral maxima ($\lambda_{abs,\ max}$ and $\lambda_{em,\ max}$), the full width at half maximum of the absorption ($fwhm_{abs}$) and the fluorescence emission ($fwhm_{em}$) bands, and the Stokes shifts. Relative fluorescence quantum yields were calculated using diluted solutions, with an absorbance between 0.02 and 0.05 at the used excitation wavelength, and a fluorescein standard (fluorescein in EtOH, Φ_f = 0.79, λ_{ex} = 425 nm). The quantum yield of the measured dye (Φ_x) was calculated using formula 1, where Φ_{st} is the quantum yield of the standard, F_x and F_{st} are the integrated fluorescence intensities of the measured dye and the standard, A_x and A_{st} are the absorbances of the measured dye and the standard at their excitation wavelengths and n_x and n_{st} are the refractive indexes of the solvents in which the measured dye and standard were diluted in. Measurements were performed using 10 mm optical path length cuvettes under right-angle arrangement. All spectroscopic measurements were done on non-degassed samples at 20 °C.

$$\phi_x = \phi_{st}\left[\frac{F_x/A_x}{F_{st}/A_{st}}\right]\left[\frac{n_x}{n_{st}}\right]^2 \quad (1)$$

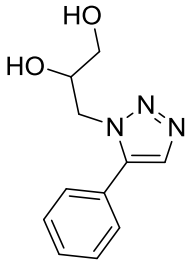
(1) (a) Tanno, M.; Sueyoshi, S.; Kamiya, S. *Chem. Pharm. Bull.* **1982**, *30*, 3125–3132. (b) Lamara, K.; Smalley, R. K. *Tetrahedron* **1991**, *47*, 2217–2290.

General triazolization procedure



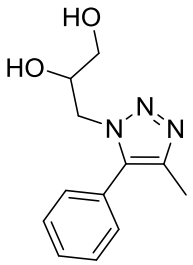
To an oven-dried screw-capped reaction tube equipped with a magnetic stirring bar was added *p*-nitrophenyl azide (90.3 mg, 0.55 mmol, 1.1 equiv), the aryl ketone **9** (0.5 mmol, 1 equiv) and 4 Å molecular sieves (60 mg). This mixture was dissolved in 1,4-dioxane (2.5 mL) and 3-aminopropane-1,2-diol **8** (0.05 mL, 0.6 mmol, 1.2 equiv) as well as acetic acid (8.6 µL, 0.15 mmol, 30 mol%) were added to this solution. After stirring the reaction mixture at 100 °C for the indicated time, it was cooled to room temperature and directly purified by column chromatography.

3-(5-Phenyl-1H-1,2,3-triazol-1-yl)propane-1,2-diol 10a



Prepared according to the triazolization procedure using acetophenone **9a** (58 µL, 0.5 mmol). After 45 hours the reaction was cooled to room temperature and directly purified by column chromatography (silica; CH_2Cl_2 to ethyl acetate) providing a yellow oil (65.9 mg, 60%). Mp: product is not crystalline; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.53 – 7.40 (m, 5H), 4.40 (d, *J* = 5.9 Hz, 2H), 4.35 – 4.26 (m, 1H), 3.71 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.60 (dd, *J* = 11.6, 5.1 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.3, 132.8, 129.8, 129.2, 129.2, 126.6, 70.8, 64.0, 50.8 ppm; HRMS (ESI-TOF, *m/z*): $[M + H]^+$ calculated for $C_{11}H_{14}N_3O_2$ 220.1086, found 220.1081; $[2M + H]^+$ calculated for $C_{22}H_{27}N_6O_4$ 439.2094, found 439.2083; $[2M + Na]^+$ calculated for $C_{22}H_{26}N_6NaO_4$ 461.1914, found 461.1900.

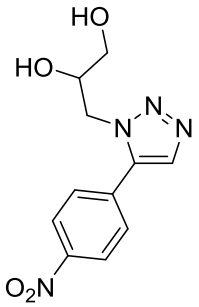
3-(4-Methyl-5-phenyl-1H-1,2,3-triazol-1-yl)propane-1,2-diol 10b



Prepared according to the triazolization procedure using propiophenone **9b** (66.5 µL, 0.5 mmol). After 44 hours the reaction was cooled to room temperature and directly purified by column

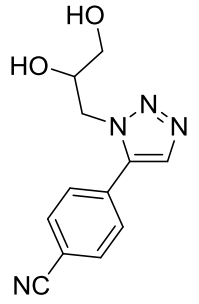
chromatography (silica; CH_2Cl_2 to ethyl acetate) providing a dark yellow solid (36.9 mg, 32%). Mp 97 – 100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.41 (m, 3H), 7.37 (d, *J* = 6.8 Hz, 2H), 4.29 (d, *J* = 7.1 Hz, 2H), 4.27 – 4.20 (m, 1H), 3.68 (dd, *J* = 11.6, 3.9 Hz, 1H), 3.57 (dd, *J* = 11.6, 5.0 Hz, 1H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 135.7, 129.8, 129.5, 129.2, 127.1, 70.7, 64.0, 50.9, 10.6 ppm; HRMS (ESI-TOF, *m/z*): $[M + H]^+$ calculated for $C_{12}H_{16}N_3O_2$ 234.1242, found 234.1245; $[M + Na]^+$ calculated for $C_{12}H_{15}N_3NaO_2$ 256.1062, found 256.1058; $[2M + H]^+$ calculated for $C_{24}H_{31}N_6O_4$ 467.2406, found 467.2407; $[2M + Na]^+$ calculated for $C_{24}H_{30}N_6NaO_4$ 489.2226, found 489.2223.

3-(5-(4-Nitrophenyl)-1H-1,2,3-triazol-1-yl)propane-1,2-diol 10c



Prepared according to the triazolization procedure using 4'-nitroacetophenone **9c** (82.6 mg, 0.5 mmol). After 46 hours the reaction was cooled to room temperature and directly purified by column chromatography (silica; CH_2Cl_2 to CH_2Cl_2/MeOH; 9:1 v/v) providing an orange solid (50.0 mg, 38%). Mp 144 – 147 °C; ^{1}H NMR (300 MHz, CD_3OD): δ 8.38 (dt, *J* = 8.9, 2.2 Hz, 2H), 7.99 – 7.88 (m, 3H), 4.62 (dd, *J* = 14.1, 3.6 Hz, 1H), 4.42 (dd, *J* = 14.1, 8.7 Hz, 1H), 4.18 – 4.09 (m, 1H), 3.57 (d, *J* = 5.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CD_3OD): δ 149.8, 139.1, 134.7, 134.3, 131.6, 125.1, 72.2, 64.9, 52.5 ppm; HRMS (ESI-TOF, *m/z*): $[M + H]^+$ calculated for $C_{11}H_{13}N_4O_4$ 265.0937, found 265.0938; $[M + Na]^+$ calculated for $C_{11}H_{12}N_4NaO_4$ 287.0757, found 287.0760.

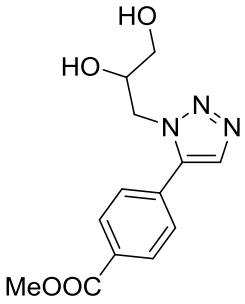
4-(1-(2,3-Dihydroxypropyl)-1H-1,2,3-triazol-5-yl)benzonitrile 10d



Prepared according to the triazolization procedure using 4-acetylbenzonitrile **9d** (72.6 mg, 0.5 mmol). After 45 hours the reaction was cooled to room temperature and directly purified by column chromatography (silica; CH_2Cl_2 to CH_2Cl_2/MeOH; 92:8 v/v) providing a gray solid (53.4 mg, 44%). Mp 119 – 122 °C; ^{1}H NMR (300 MHz, CD_3OD): δ 7.94 – 7.81 (m, 5H), 4.59 (dd, *J* = 14.1, 3.7 Hz, 1H), 4.39 (dd, *J* = 14.1, 8.7 Hz, 1H), 4.17 – 4.08 (m, 1H), 3.56 (d, *J* = 5.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CD_3OD): δ 139.3, 134.1, 133.9, 133.0, 131.3, 119.2, 114.3, 72.2, 64.9, 52.4 ppm; HRMS (ESI-TOF, *m/z*): [M +

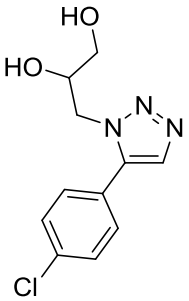
H]$^+$ calculated for $C_{12}H_{13}N_4O_2$ 245.1038, found 245.1042; [M + Na]$^+$ calculated for $C_{12}H_{12}N_4NaO_2$ 267.0858, found 267.0861.

Methyl 4-(1-(2,3-dihydroxypropyl)-1H-1,2,3-triazol-5-yl)benzoate 10e



Prepared according to the triazolization procedure using methyl 4-acetylbenzoate **9e** (89.1 mg, 0.5 mmol). After 47 hours the reaction was cooled to room temperature and directly purified by column chromatography (silica; CH_2Cl_2 to CH_2Cl_2/MeOH; 9:1 v/v). The resulting mixture was further purified via crystallization from a chloroform/heptane mixture by evaporation followed by filtering and washing the formed crystals with pentane. This provided the pure compound as light yellow crystals (54.7 mg, 39%). Mp 114 – 115 °C; ^{1}H NMR (300 MHz, CD_3OD): δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.87 (s, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 4.59 (dd, *J* = 14.0, 3.8 Hz, 1H), 4.41 (dd, *J* = 14.0, 8.6 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.94 (s, 3H), 3.56 (d, *J* = 5.2 Hz, 2H) ppm; ^{13}C NMR (75 MHz, CD_3OD): δ 167.8, 139.9, 133.9, 132.9, 132.2, 131.1, 130.6, 72.1, 64.9, 52.9, 52.4 ppm; HRMS (ESI-TOF, *m/z*): [M + H]$^+$ calculated for $C_{13}H_{16}N_3O_4$ 278.1141, found 278.1129; [M + Na]$^+$ calculated for $C_{13}H_{15}N_3NaO_4$ 300.0961, found 300.0948; [M + K]$^+$ calculated for $C_{13}H_{15}KN_3O_4$ 316.0700, found 316.0690; [2M + H]$^+$ calculated for $C_{26}H_{31}N_6O_8$ 555.2204, found 555.2199; [2M + Na]$^+$ calculated for $C_{26}H_{30}N_6NaO_8$ 577.2024, found 577.2015.

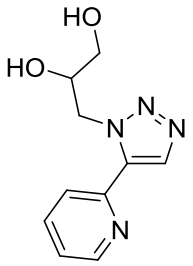
3-(5-(4-Chlorophenyl)-1H-1,2,3-triazol-1-yl)propane-1,2-diol 10f



Prepared according to the triazolization procedure using 4'-chloroacetophenone **9f** (65 µL, 0.5 mmol). After 48 hours the reaction was cooled to room temperature and directly purified by column chromatography (silica; heptane/ethyl acetate; 1:2 v/v to ethyl acetate) providing a brown sticky oil (75.4 mg, 59%). Mp: product is not crystalline; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.40 (d, *J* = 5.7 Hz, 2H), 4.33 – 4.27 (m, 1H), 3.76 (dd, *J* = 11.5, 4.2 Hz, 1H), 3.66 (dd, *J* = 11.5, 4.9 Hz, 1H), 3.50 (s, br, 1H), 2.35 (s, br, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 136.3, 133.2, 130.6, 129.7, 125.1, 70.7, 64.0, 50.7 ppm; HRMS (ESI-TOF, *m/z*): [M +

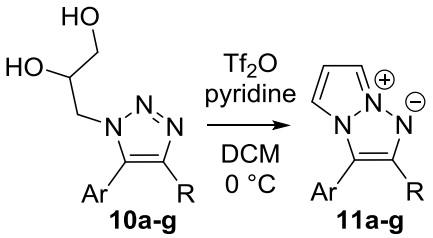
H]$^+$ calculated for $C_{11}H_{13}ClN_3O_2$ 254.0696, found 254.0693; [M + Na]$^+$ calculated for $C_{11}H_{12}ClN_3NaO_2$ 276.0516, found 276.0509; [M + K]$^+$ calculated for $C_{11}H_{12}ClKN_3O_2$ 292.0255, found 292.0249; [2M + H]$^+$ calculated for $C_{22}H_{25}Cl_2N6O_4$ 507.1314, found 507.1315; [2M + Na]$^+$ calculated for $C_{22}H_{24}Cl_2N_6NaO_4$ 529.1134, found 529.1127.

3-(5-(Pyridin-2-yl)-1H-1,2,3-triazol-1-yl)propane-1,2-diol 10g



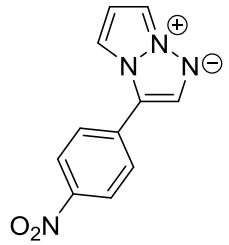
Prepared according to the triazolization procedure using 2-acetylpyridine **9f** (56 µL, 0.5 mmol). After 24 hours the reaction was cooled to room temperature and directly purified by column chromatography (silica; CH_2Cl_2 to CH_2Cl_2/MeOH; 95:5 v/v) providing yellow crystals (91.8 mg, 83%). Mp 90 – 92 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.69 (ddd, *J* = 5.0, 1.7, 0.9 Hz, 1H), 8.00 (s, 1H), 7.93 (td, *J* = 7.8, 1.8 Hz, 1H), 7.70 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.45 (ddd, *J* = 7.6, 5.0, 1.1 Hz, 1H), 5.75 (s, br, 1H), 4.87 (d, *J* = 5.4 Hz, 2H), 4.38 – 4.29 (m, 1H), 3.66 (d, *J* = 3.2 Hz, 2H), 3.47 (s, br, 1H) ppm; ^{13}C NMR (75 MHz, CD_3OD): δ 150.5, 147.9, 139.3, 138.3, 134.4, 125.2, 125.1, 72.6, 64.9, 53.3 ppm; HRMS (ESI-TOF, *m/z*): [M + H]$^+$ calculated for $C_{10}H_{13}N_4O_2$ 221.1038, found 221.1043; [M + Na]$^+$ calculated for $C_{10}H_{12}N_4NaO_2$ 243.0858, found 243.0863; [M + K]$^+$ calculated for $C_{10}H_{12}KN_4O_2$ 259.0597, found 259.0604; [2M + H]$^+$ calculated for $C_{20}H_{25}N_8O_4$ 441.1998, found 441.1998; [2M + Na]$^+$ calculated for $C_{20}H_{24}N_8NaO_4$ 463.1818, found 463.1813.

General procedure for the preparation of 3-aryl 1,3a,6a-triazapentalenes



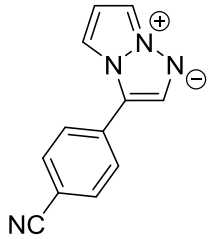
The synthesized triazole **10** (0.1 mmol) was dissolved in DCM (1 mL) and cooled in an ice bath. To this solution was added pyridine (81 µL, 1 mmol, 10 equiv) followed by dropwise addition of triflic anhydride (50 µL, 0.3 mmol, 3 equiv). This reaction mixture was stirred at 0 °C for the indicated time in the presence of air. Afterwards the reaction was quenched by addition of MeOH (24 µL, 0.6 mmol, 6 equiv) and stirred at room temperature until TLC analysis showed that the intermediate was completely converted to a colored compound. The crude reaction mixture was then directly purified by column chromatography and the eluates containing product were evaporated to dryness at 30 °C.

3-(4-Nitrophenyl)-1,3a,6a-triazapentalene 11c



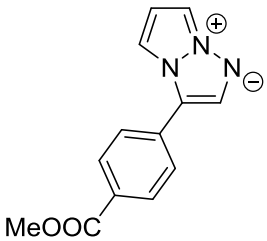
Prepared following the general triazapentalene synthesis procedure using 3-(5-(4-nitrophenyl)-1H-1,2,3-triazol-1-yl)propane-1,2-diol **10c** (26.4 mg, 0.1 mmol) for 40 minutes. The crude product was directly purified by column chromatography (silica; CH_2Cl_2 to CH_2Cl_2/MeOH; 99:1 v/v) providing a red-brown solid (15.8 mg, 69%). Mp: transition at 181 °C, partial melting point of original crystals at 211 °C, partial melting point of new crystals at 216 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, *J* = 9.0 Hz, 2H), 7.98 (d, *J* = 1.2 Hz, 1H), 7.66 (d, *J* = 3.0 Hz, 1H), 7.64 (d, *J* = 2.9 Hz, 1H), 7.56 (d, *J* = 9.1 Hz, 2H), 6.84 (td, *J* = 3.0, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 135.1, 134.6, 125.3, 120.9, 111.3, 110.1, 105.9, 104.5 ppm; HRMS (ESI-TOF, *m/z*): $[M + H]^+$ calculated for $C_{11}H_9N_4O_2$ 229.0725, found 229.0723.

3-(4-Cyanophenyl)-1,3a,6a-triazapentalene 11d



Prepared following the general triazapentalene synthesis procedure using 4-(1-(2,3-dihydroxypropyl)-1H-1,2,3-triazol-5-yl)benzonitrile **10d** (24.4 mg, 0.1 mmol) for 30 minutes. After quenching the reaction with MeOH and stirring 4.5 hours at room temperature, the crude product was directly purified by column chromatography (silica; CH_2Cl_2) providing an orange-brown solid (15.8 mg, 76%). Mp 153 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 1.2 Hz, 1H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 2.9 Hz, 1H), 7.59 (d, *J* = 3.1 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 6.82 (td, *J* = 3.0, 1.3 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.3, 133.2, 132.8, 121.5, 119.4, 111.2, 109.9, 107.3, 105.3, 103.8 ppm; HRMS (ESI-TOF, *m/z*): $[M + H]^+$ calculated for $C_{12}H_9N_4$ 209.0827, found 209.0828.

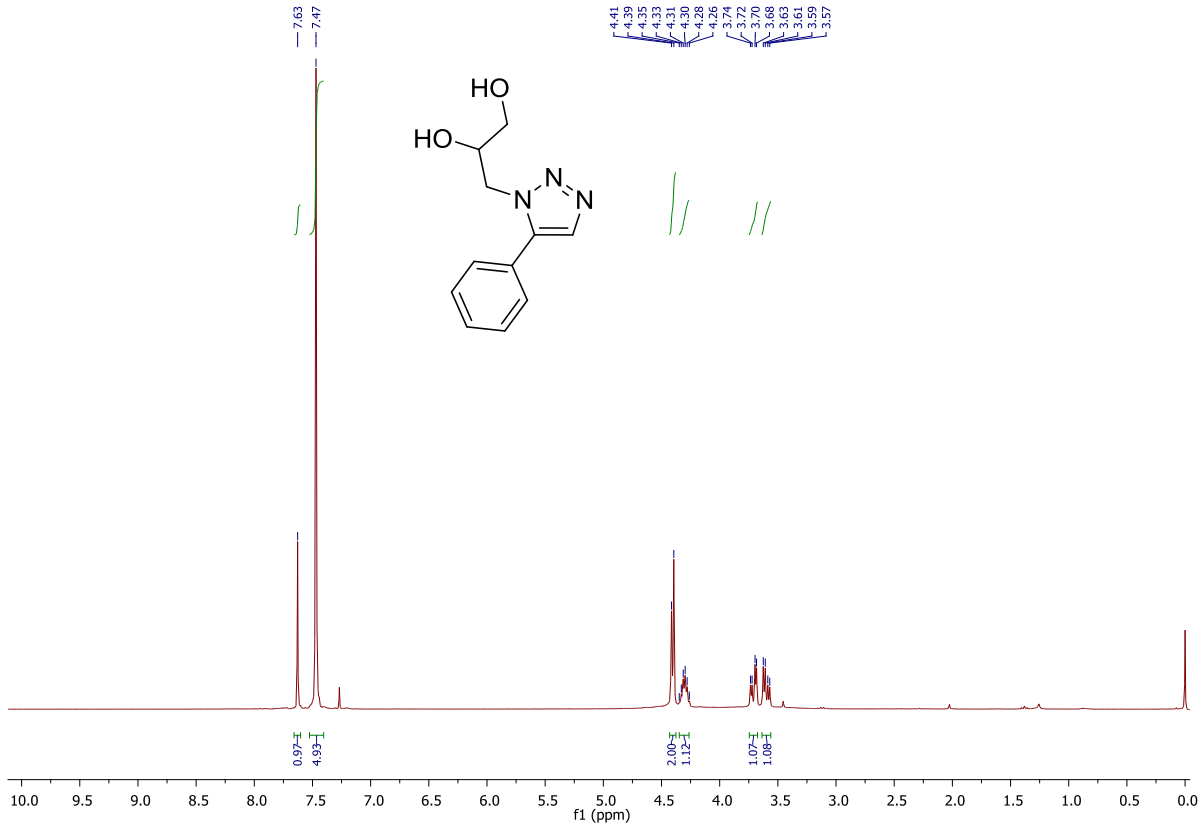
3-(4-(Methoxycarbonyl)phenyl)-1,3a,6a-triazapentalene 11e



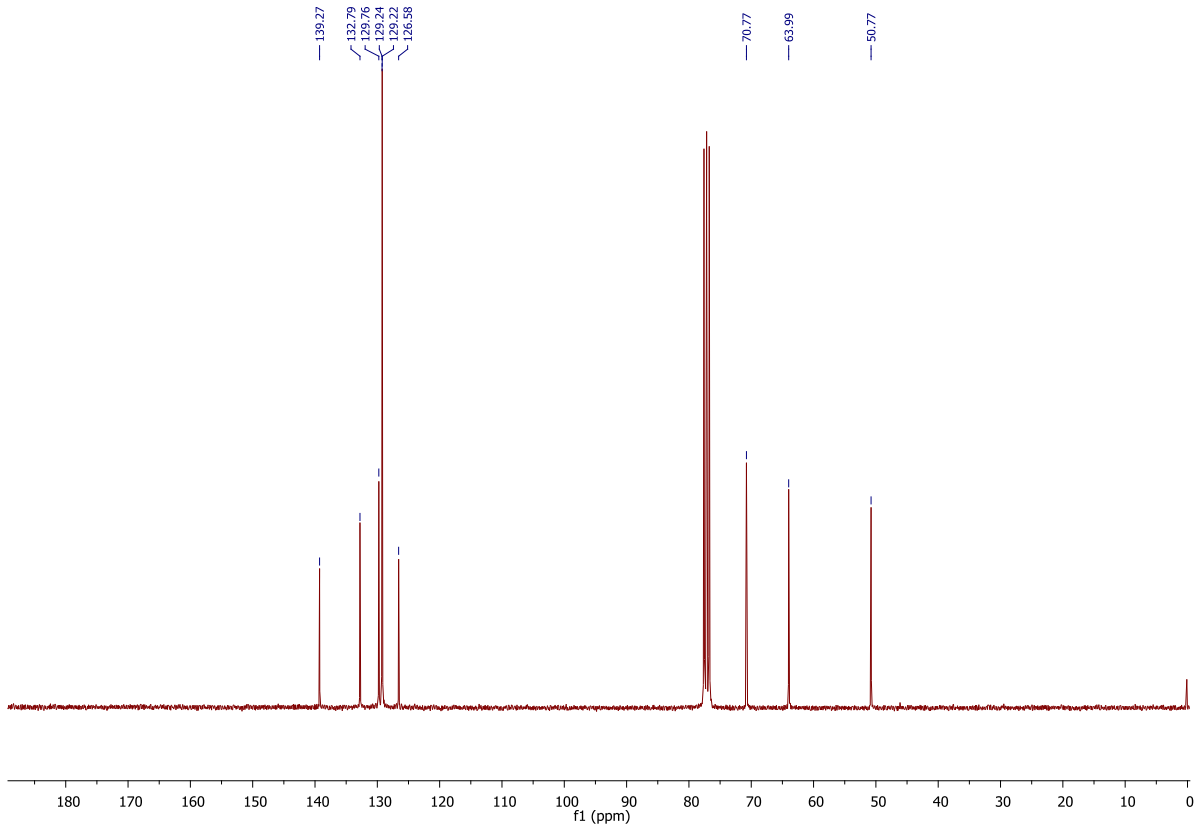
Prepared following the general triazapentalene synthesis procedure using methyl 4-(1-(2,3-dihydroxypropyl)-1H-1,2,3-triazol-5-yl)benzoate **10e** (27.7 mg, 0.1 mmol) for 30 minutes. After quenching the reaction with MeOH and stirring 5 hours at room temperature, the crude product was directly purified by column chromatography (silica; CH_2Cl_2/MeOH; 99:1 v/v) providing a yellow solid (16.9 mg, 70%). Mp 163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 1.1 Hz, 1H), 7.60 (d, *J* = 2.9 Hz, 1H), 7.57 (d, *J* = 2.8 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 6.80 (td, *J* = 2.9, 1.2 Hz, 1H), 3.93 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 133.8, 132.9, 130.8, 126.2, 121.2, 111.8, 109.7, 104.6, 103.3, 52.2 ppm; HRMS (ESI-TOF, *m/z*): $[M + H]^+$ calculated for $C_{13}H_{12}N_3O_2$ 242.0929, found 242.0931.

NMR-spectra of all new compounds

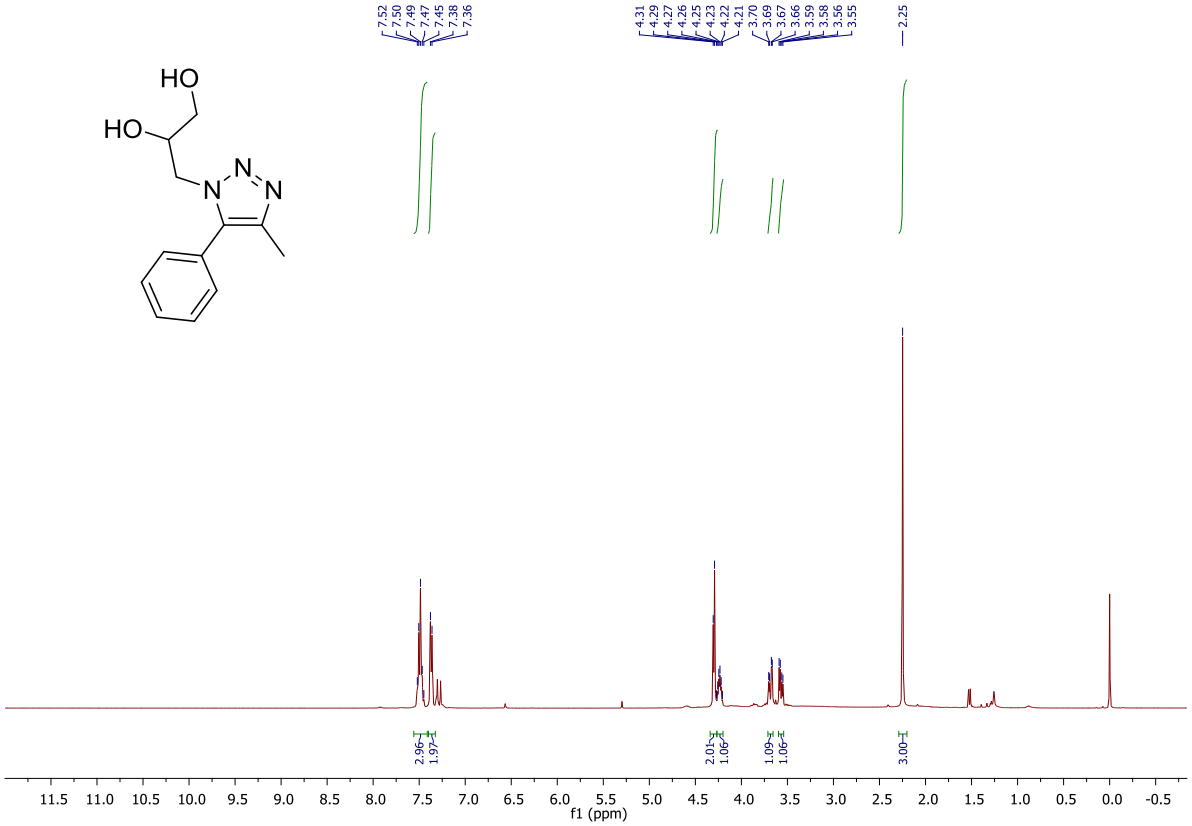
10a, ^{1}H, 300 MHz, $CDCl_3$



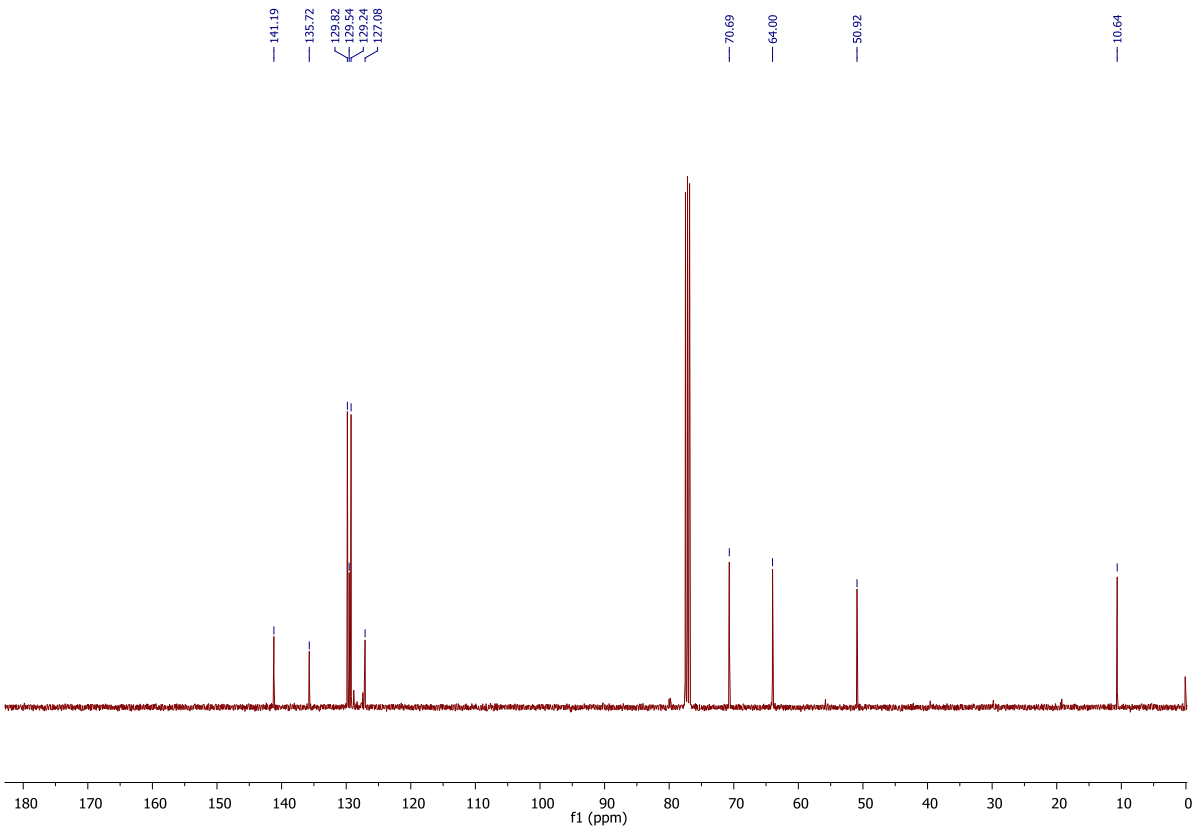
10a, ^{13}C, 75 MHz, $CDCl_3$



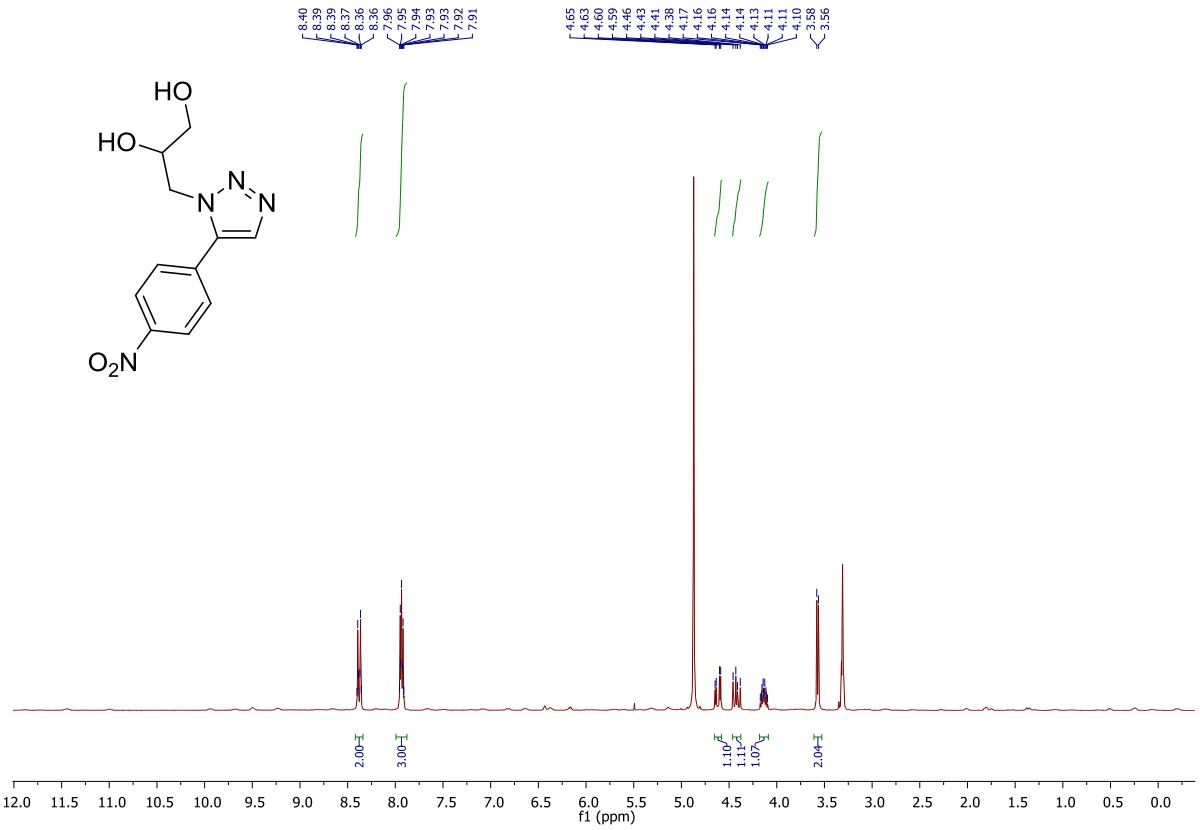
10b, ^{1}H, 400 MHz, $CDCl_3$



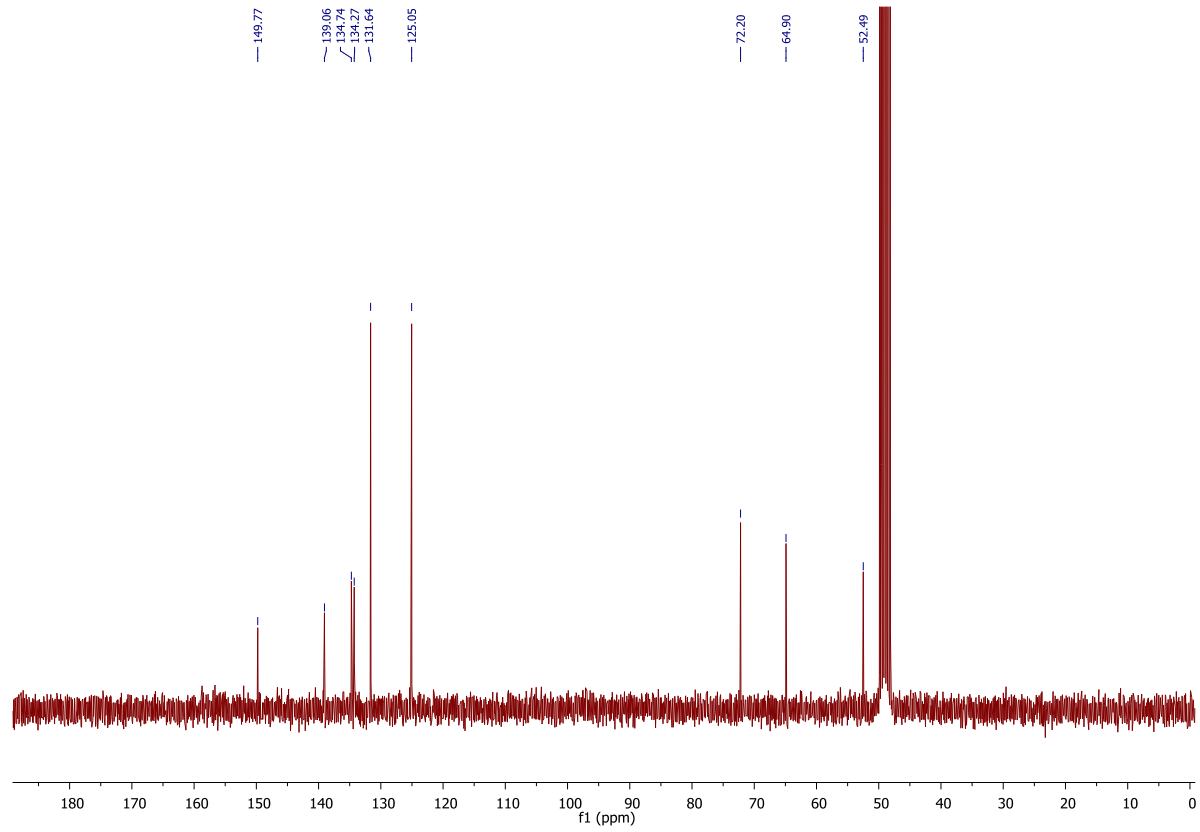
10b, ^{13}C, 100 MHz, $CDCl_3$



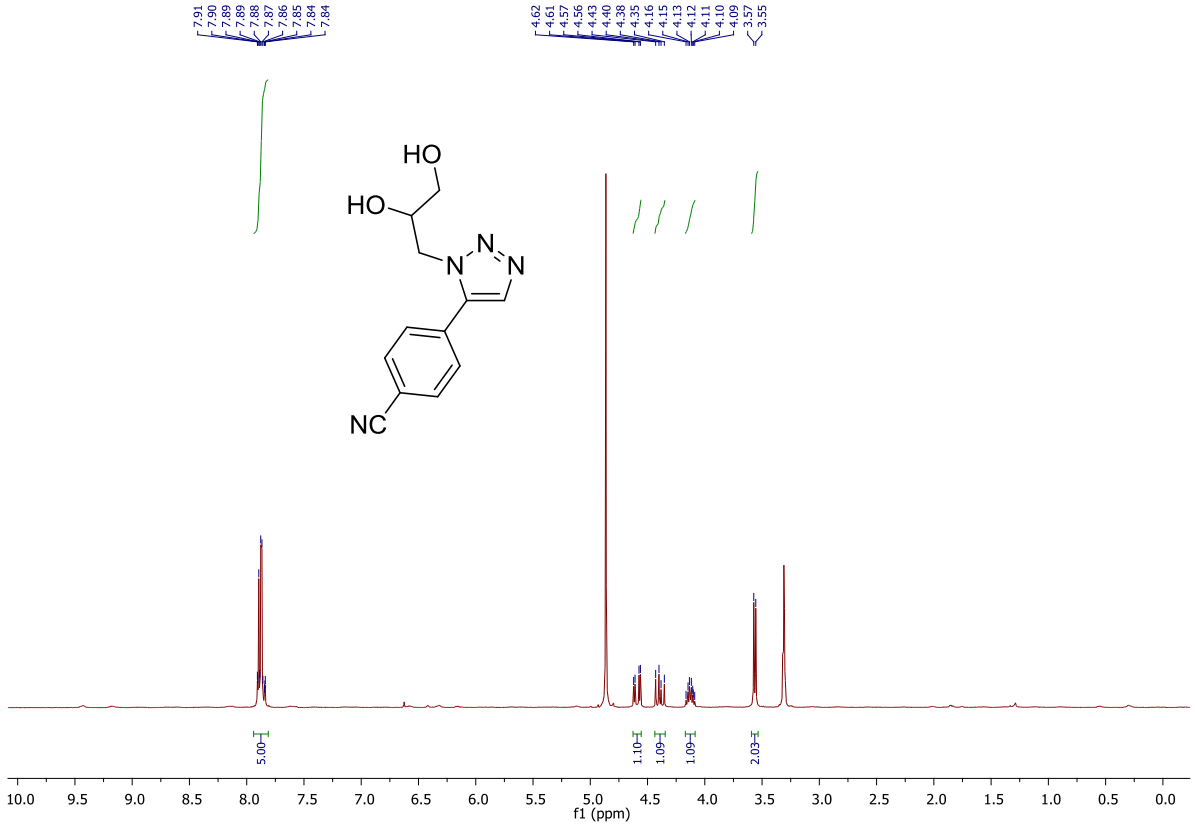
10c, ^{1}H, 300 MHz, CD_3OD



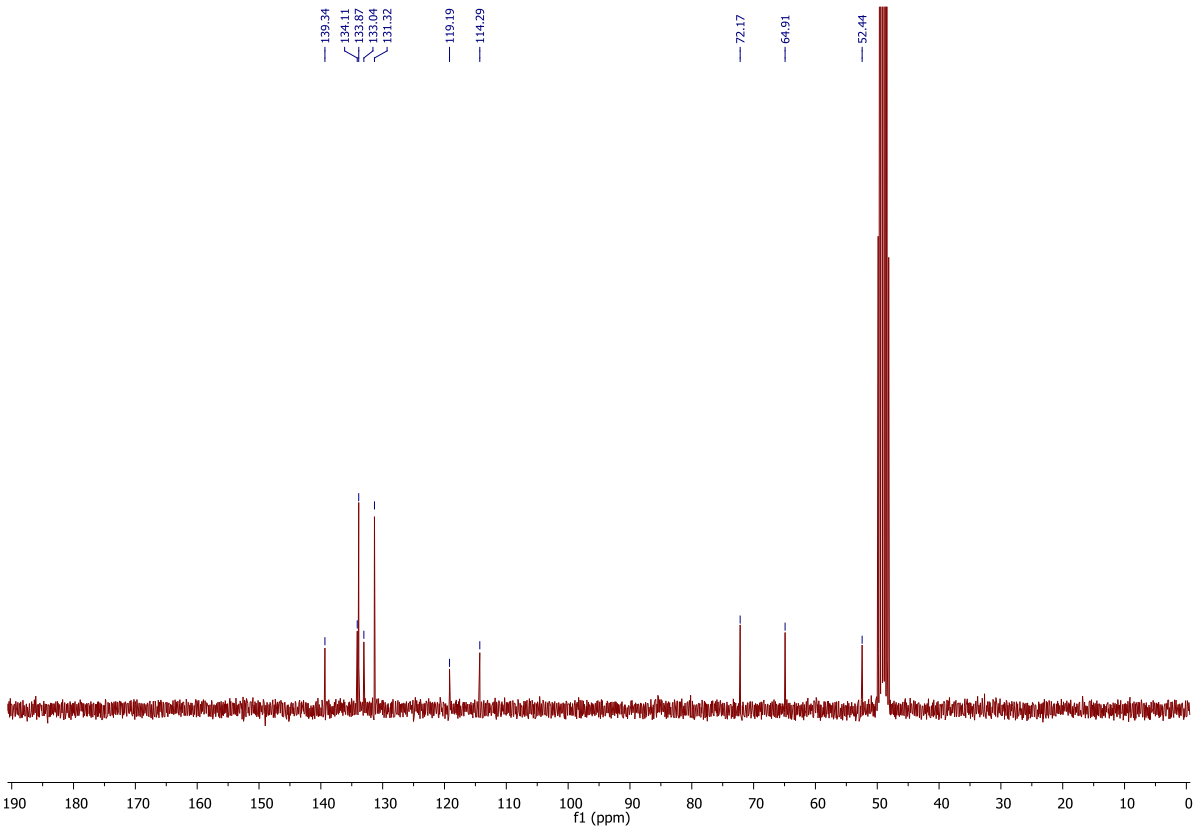
10c, ^{13}C, 75 MHz, CD_3OD



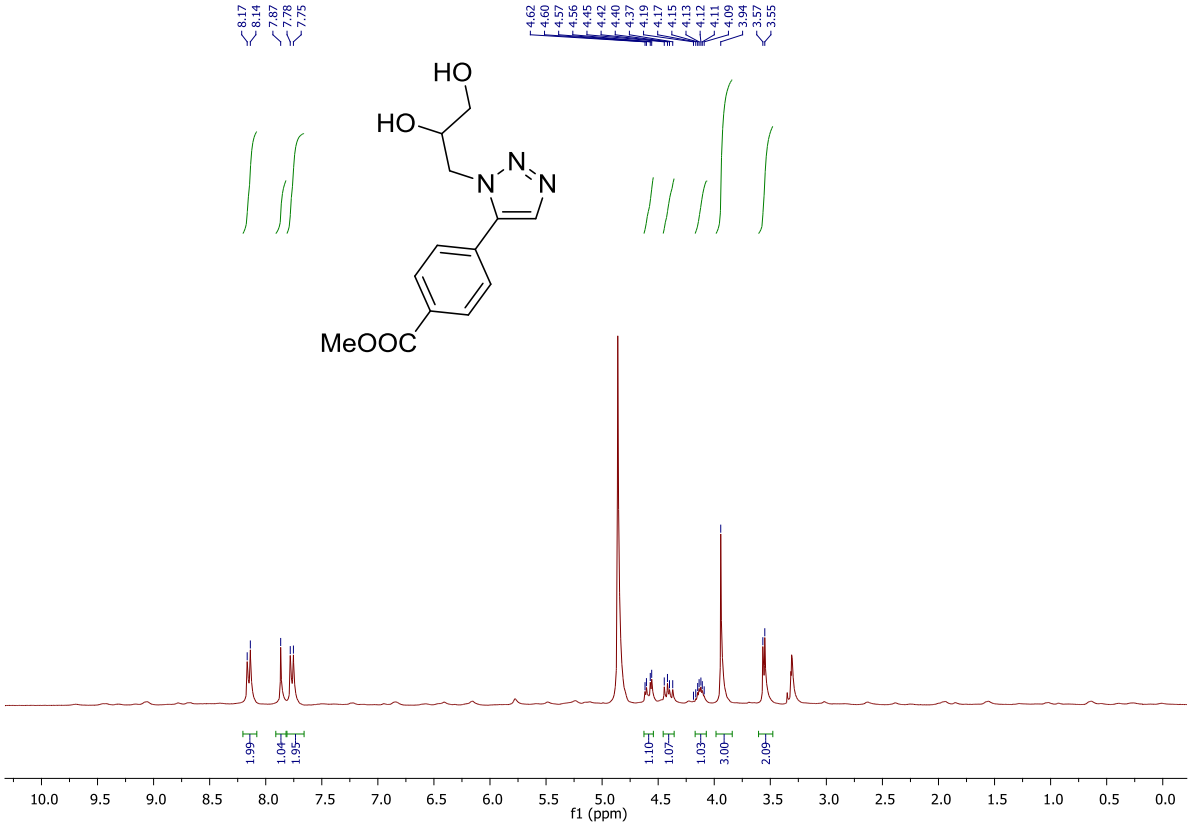
10d, ^{1}H, 300 MHz, CD_3OD



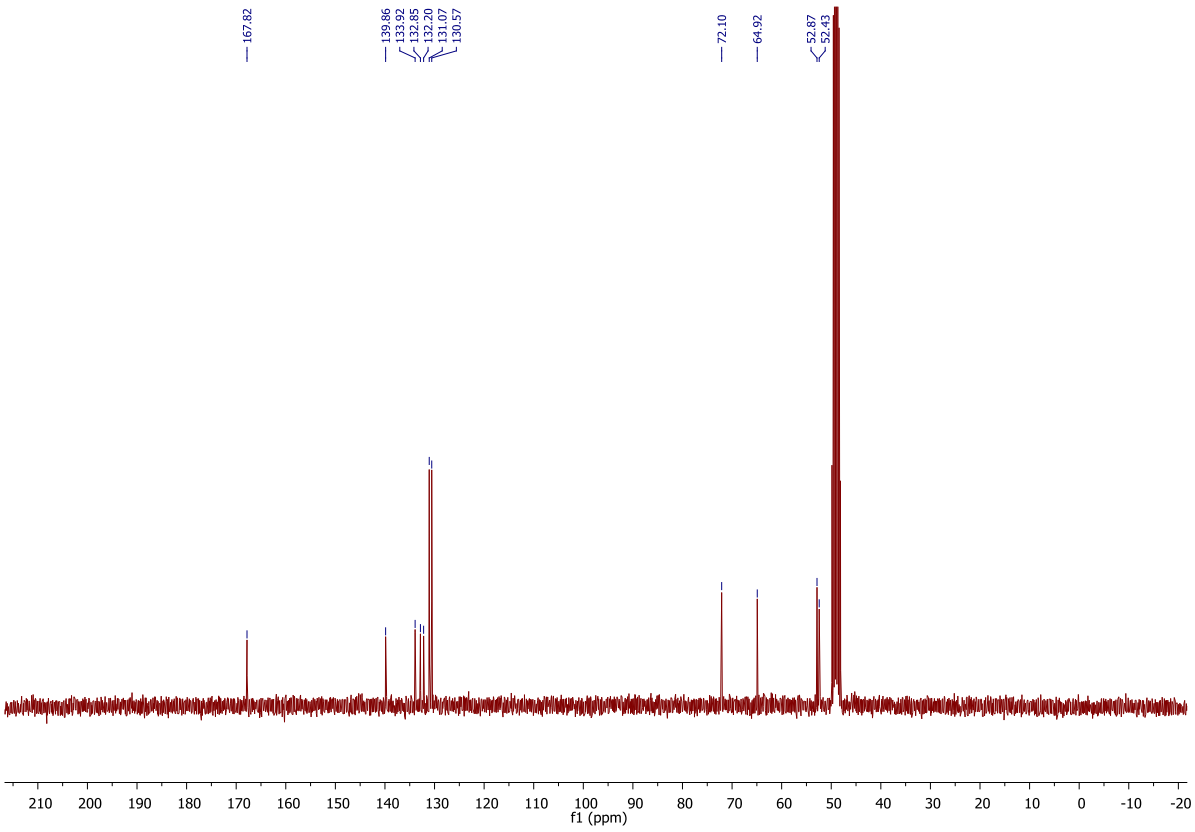
10d, ^{13}C, 75 MHz, CD_3OD



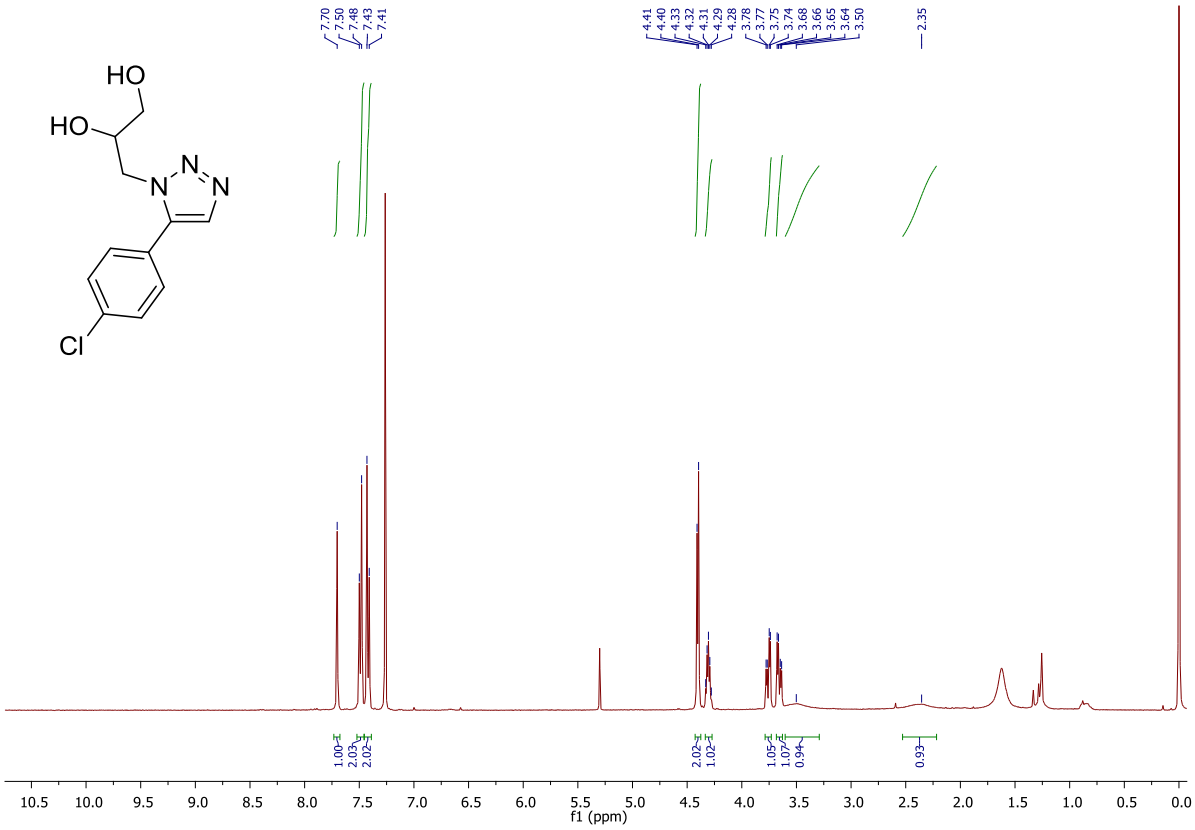
10e, ^{1}H, 300 MHz, CD_3OD



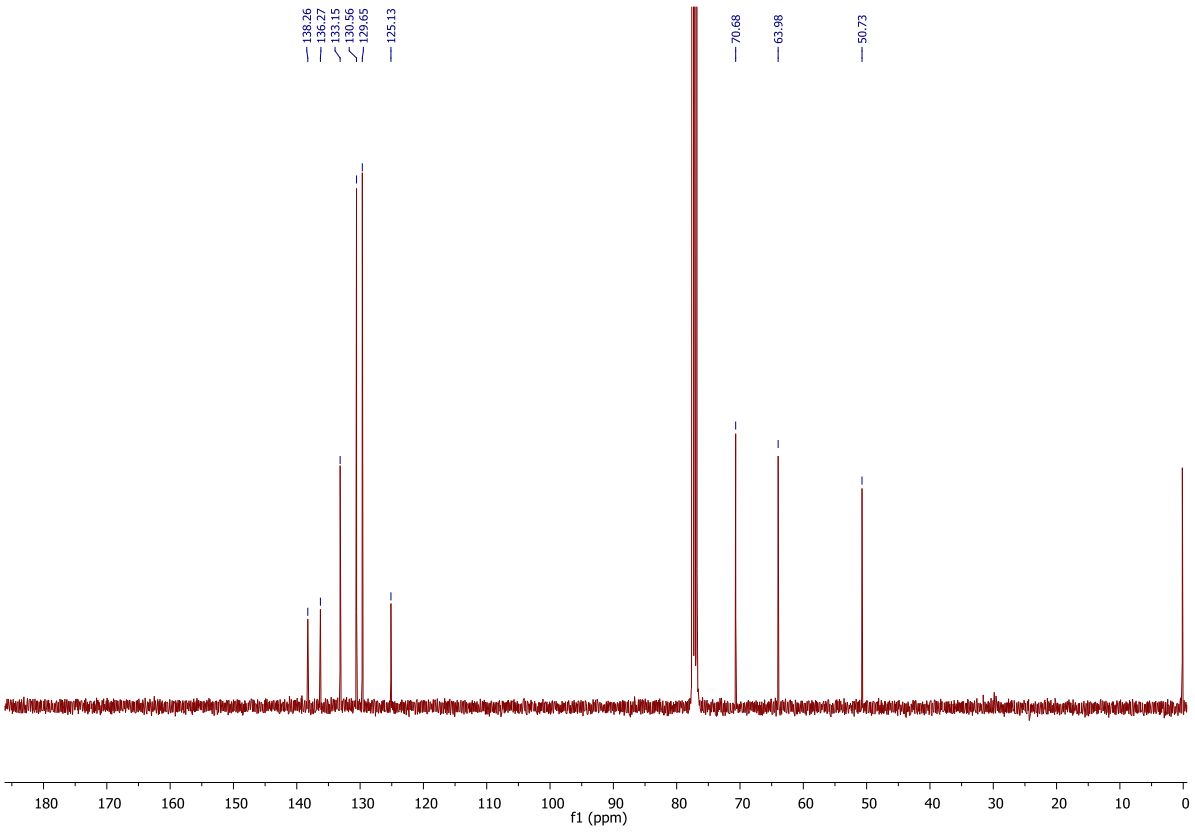
10e, ^{13}C, 75 MHz, CD_3OD



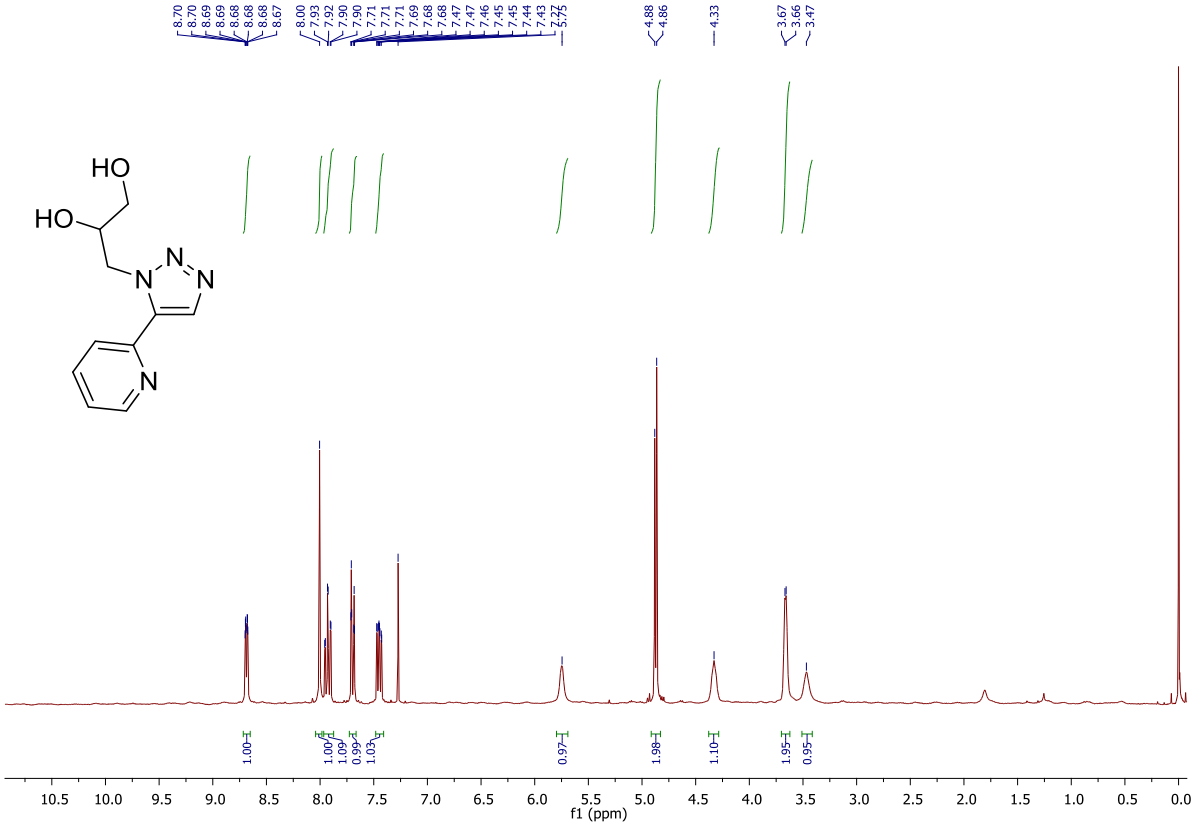
10f, ^{1}H, 400 MHz, $CDCl_3$



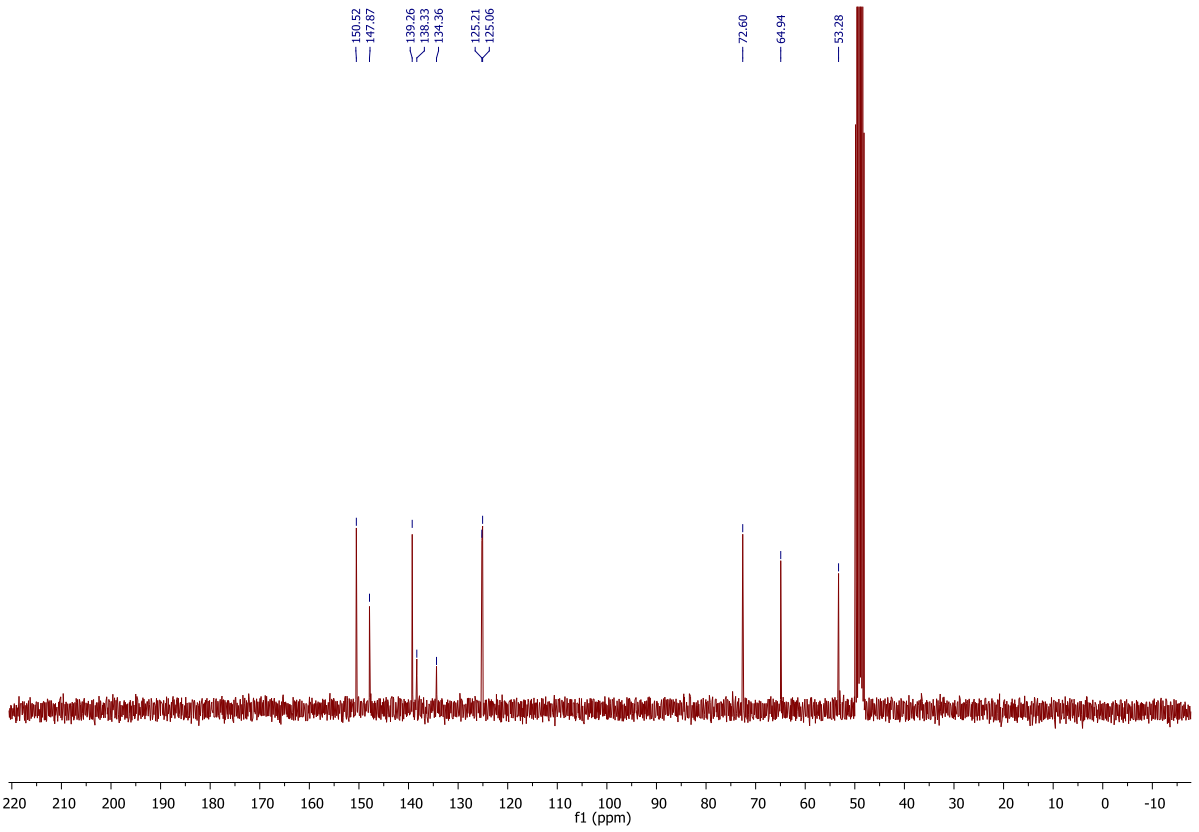
10f, ^{13}C, 100 MHz, $CDCl_3$



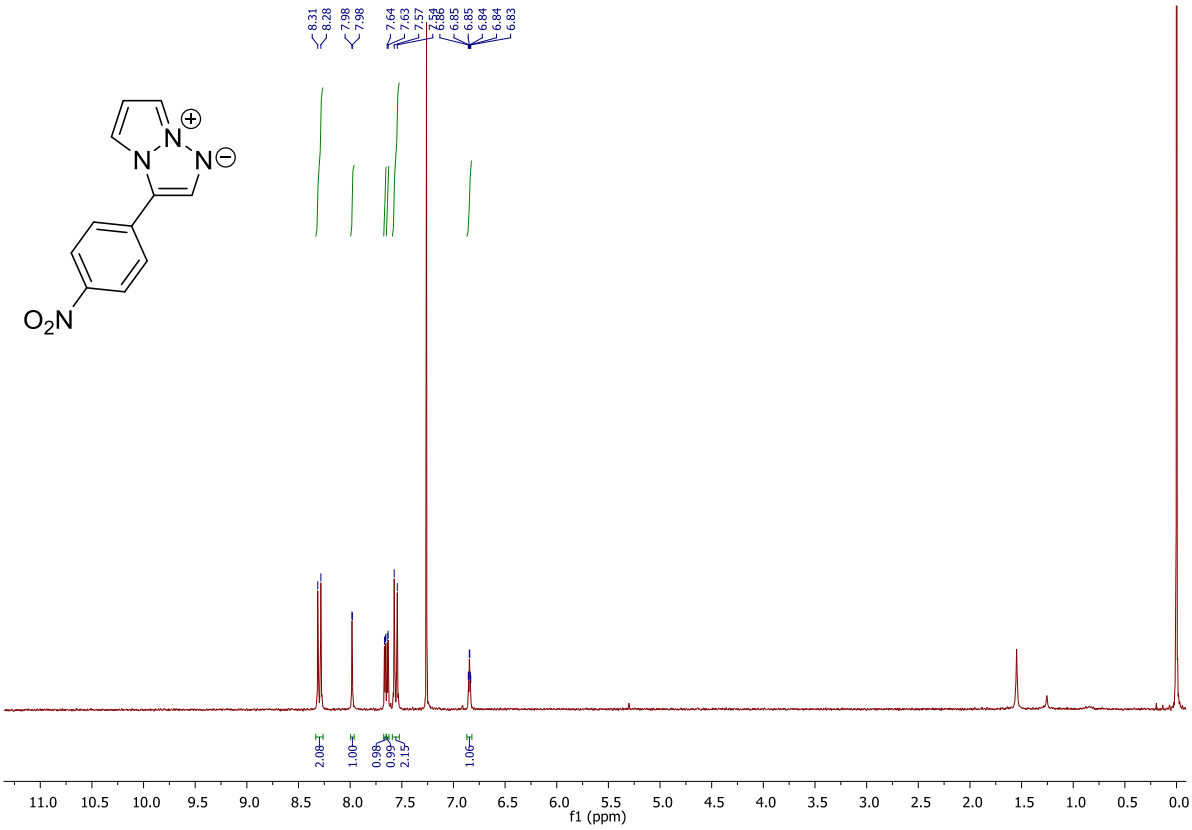
10g, ^{1}H, 300 MHz, $CDCl_3$



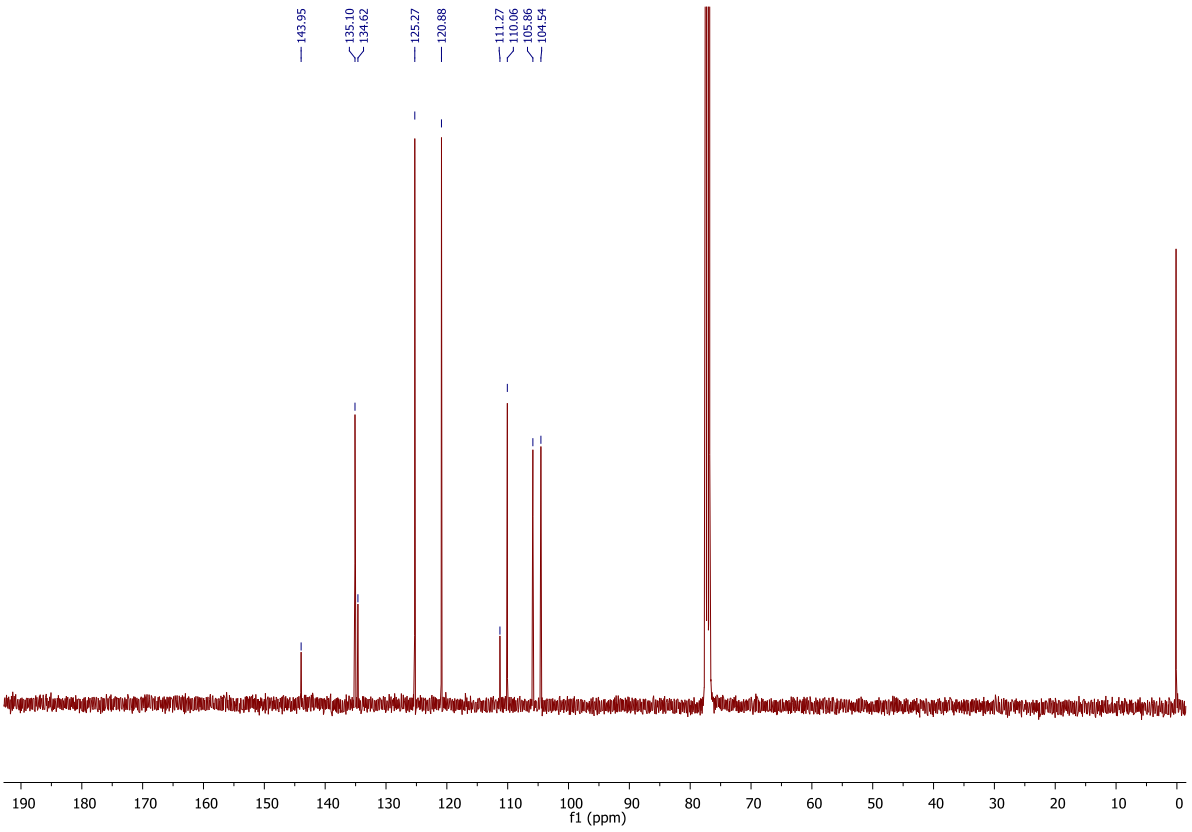
10g, ^{13}C, 75 MHz, CD_3OD



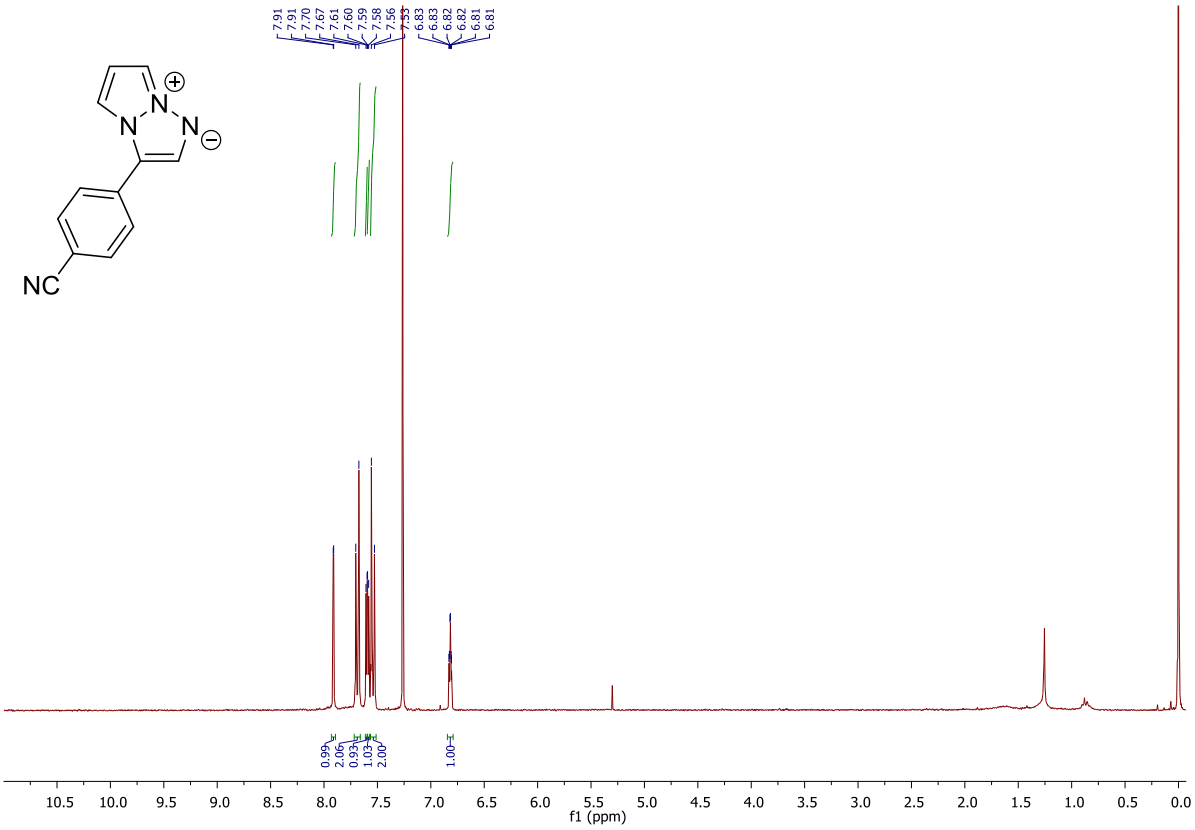
11c, ^{1}H, 300 MHz, $CDCl_3$



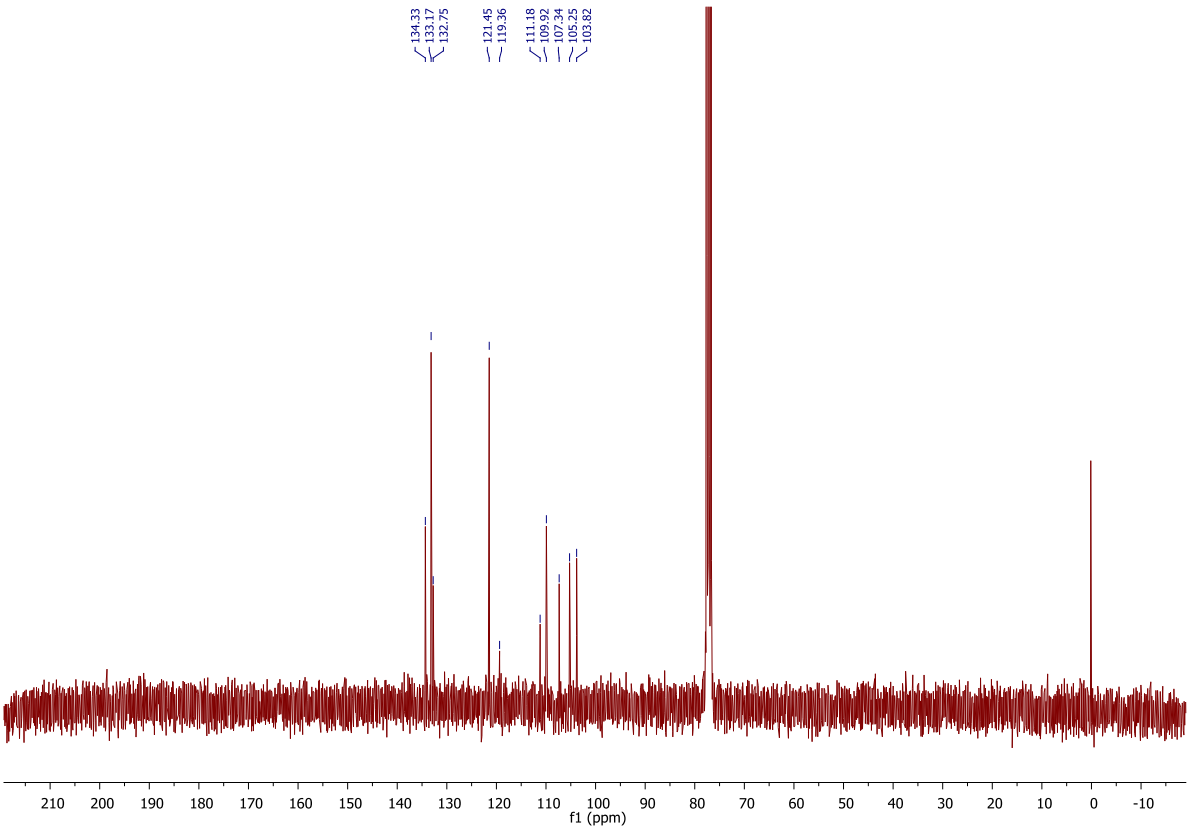
11c, ^{13}C, 100 MHz, $CDCl_3$



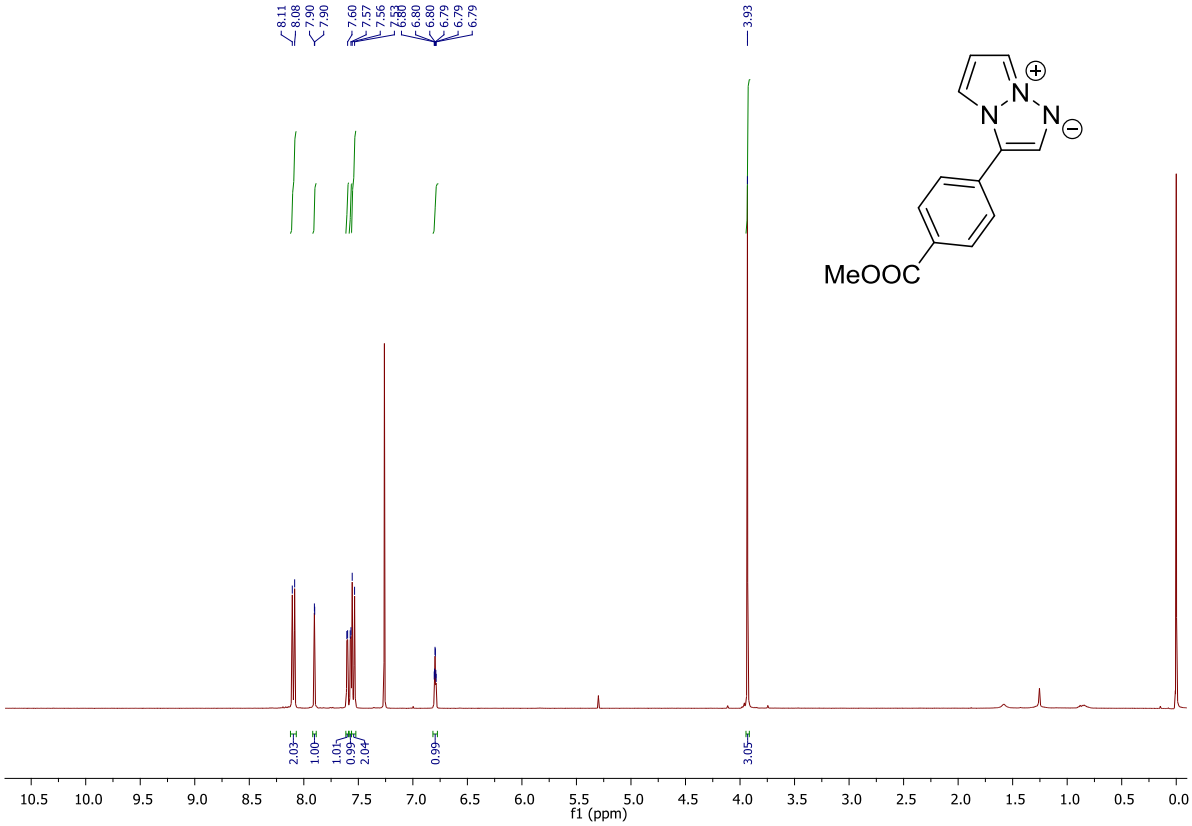
11d, ^{1}H, 300 MHz, $CDCl_3$



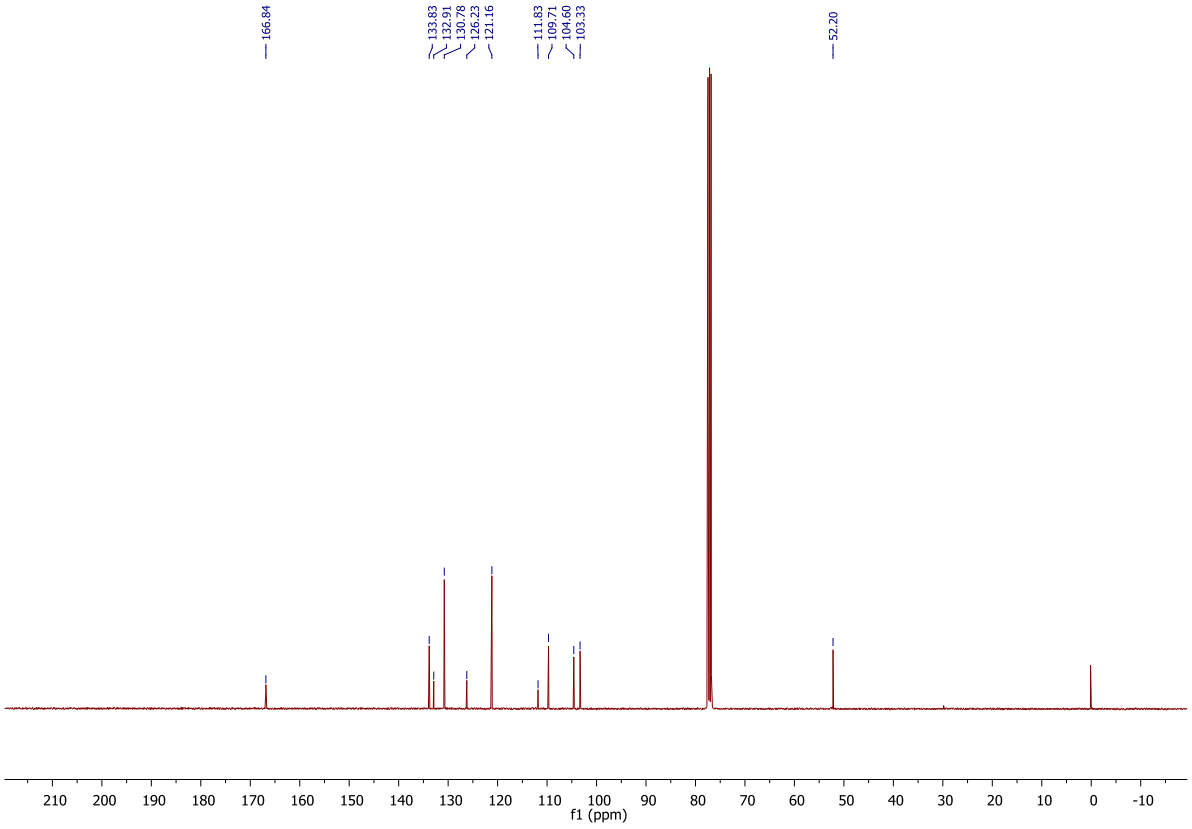
11d, ^{13}C, 75 MHz, $CDCl_3$



11e, ^{1}H, 400 MHz, $CDCl_3$



11e, ^{13}C, 100 MHz, $CDCl_3$



Characterization of crude mixtures of unstable 11a and 11b

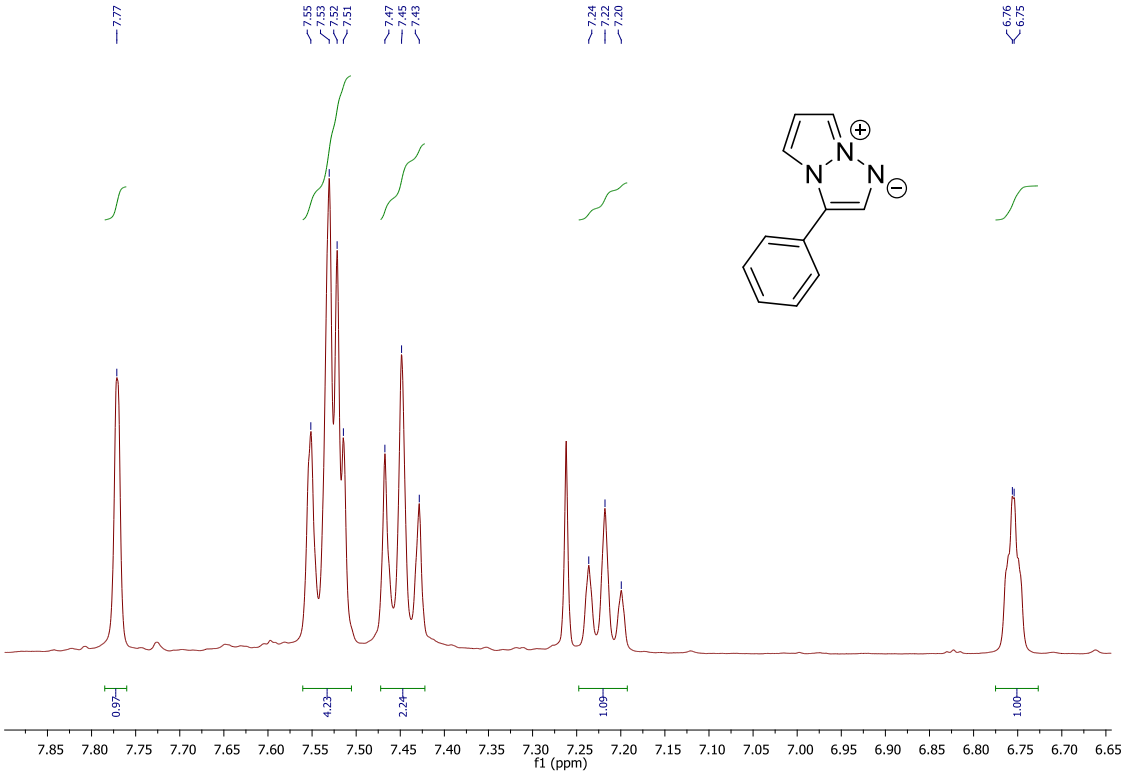


Figure S1. Aromatic region of the ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the crude mixture of triazapentalene **11a**.

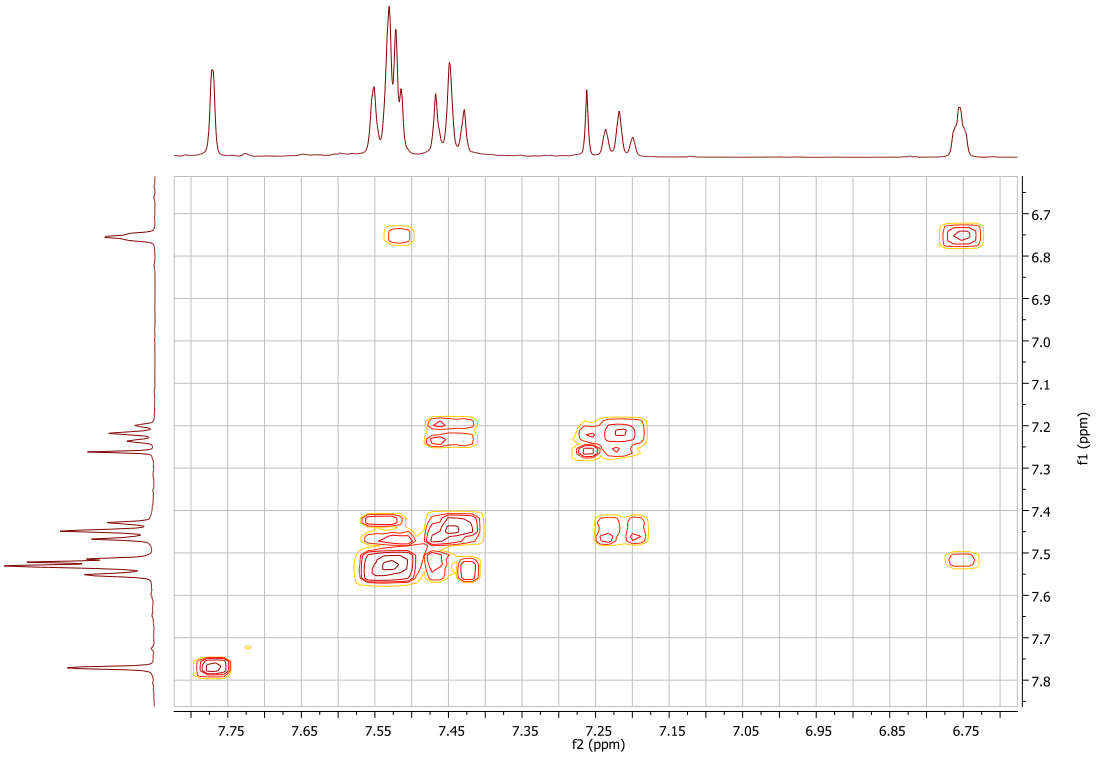


Figure S2. Aromatic region of the COSY NMR (400 MHz, $CDCl_3$) spectrum of the crude mixture of triazapentalene **11a**.

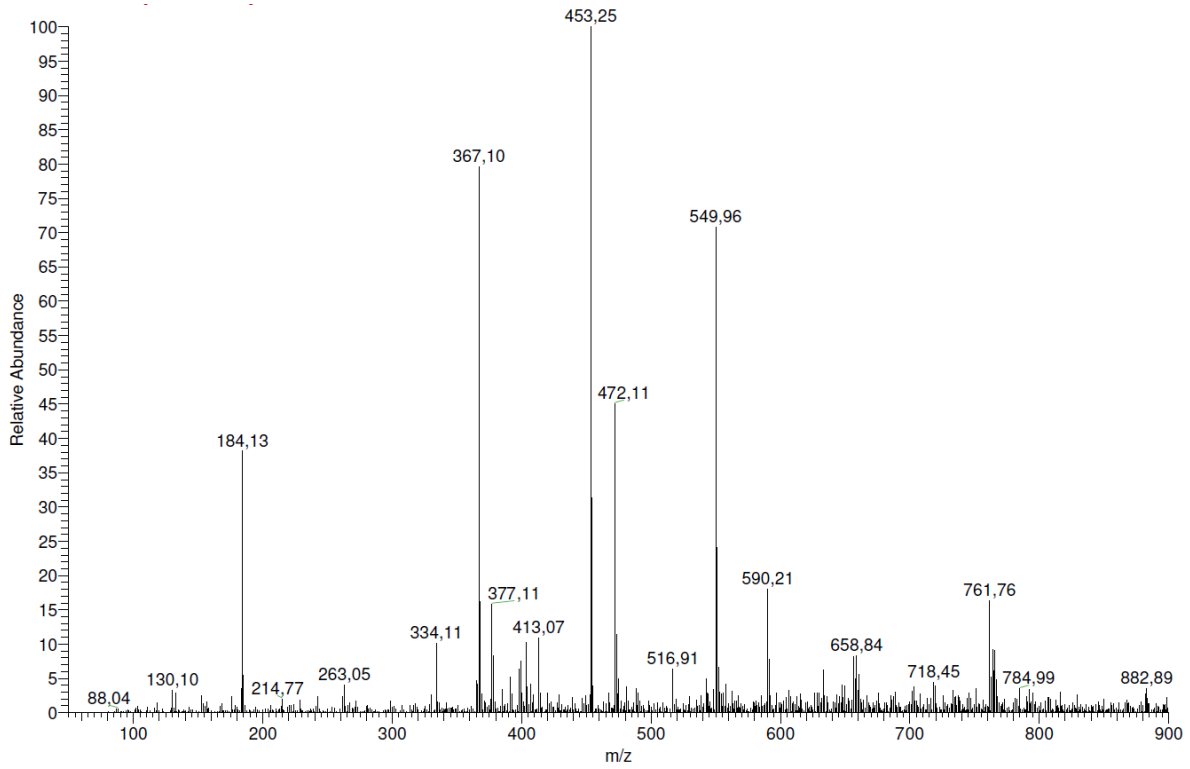


Figure S3. Mass (ESI, *m/z*) spectrum of the crude mixture of triazapentalene **11a**, peaks: 184 $[M + H]^+$, 367 $[2M + H]^+$, 550 $[3M + H]^+$.

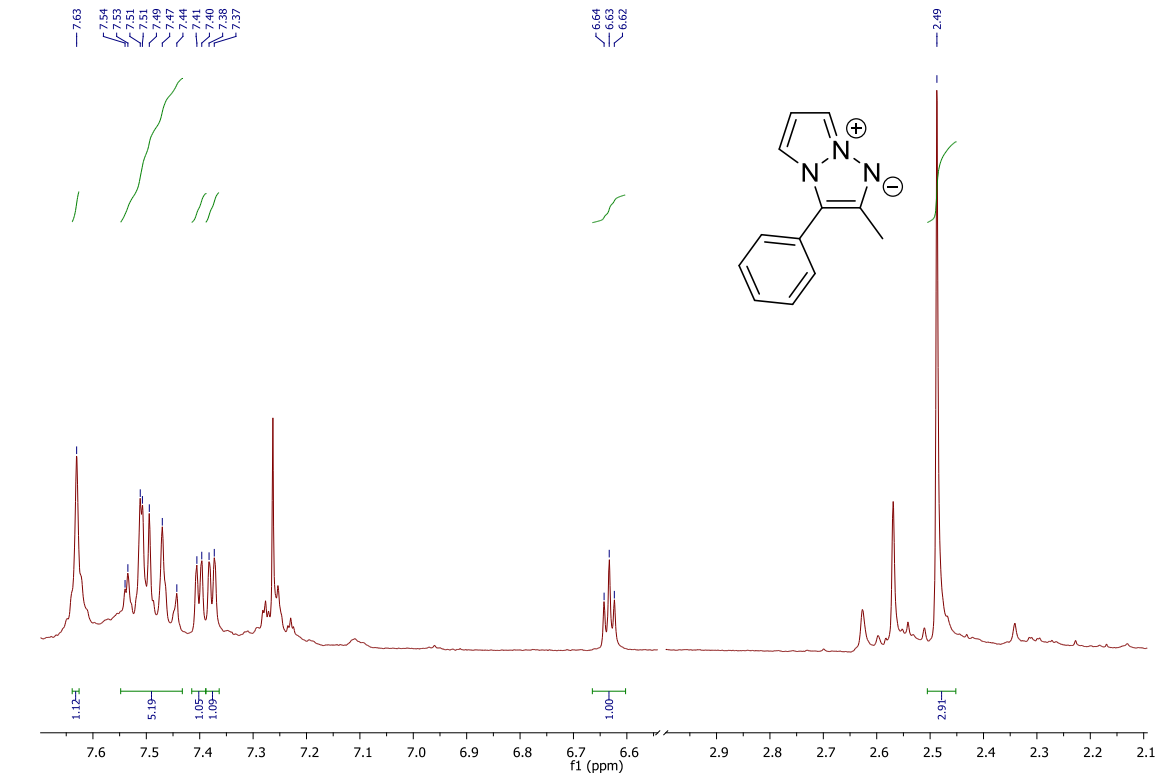


Figure S4. Aromatic and aliphatic regions of the ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of the crude mixture of triazapentalene **11b**.

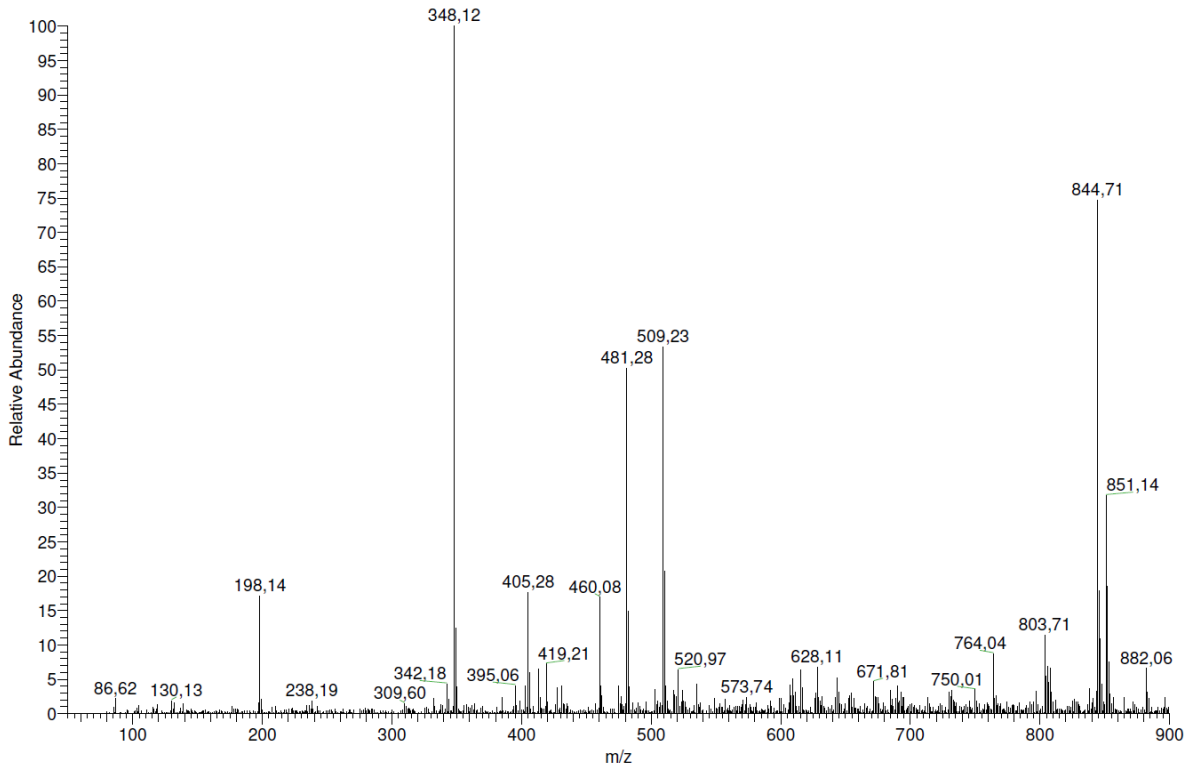


Figure S5. Mass (ESI, *m/z*) spectrum of the crude mixture of triazapentalene **11b**, peak: 198 $[M + H]^+$.

UV–vis spectroscopic data

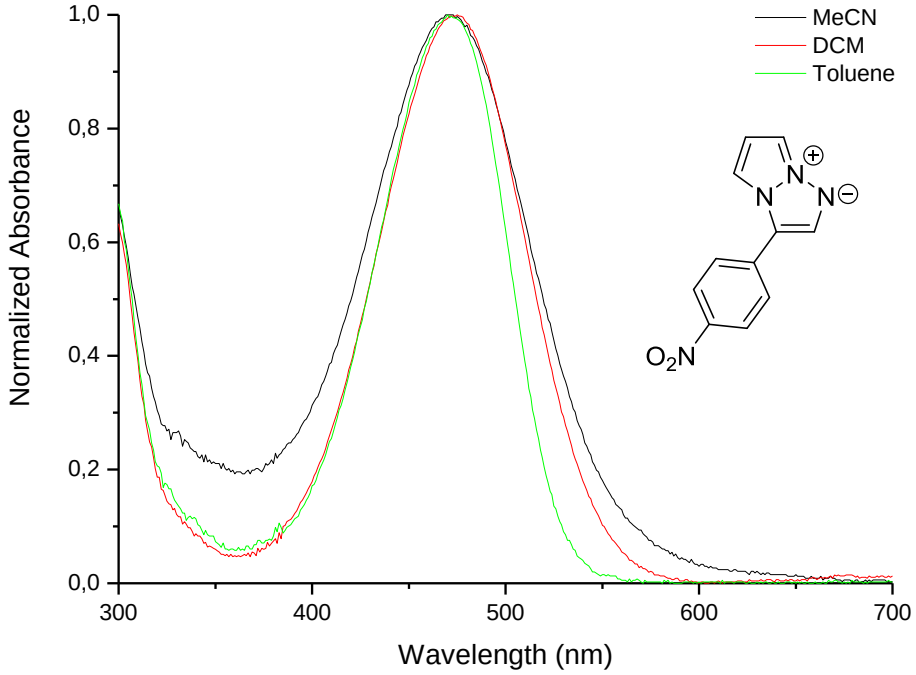


Figure S6. Normalized, visible absorption spectra of 3-(4-nitrophenyl)-1,3a,6a-triazapentalene **11c** in MeCN, DCM and toluene.

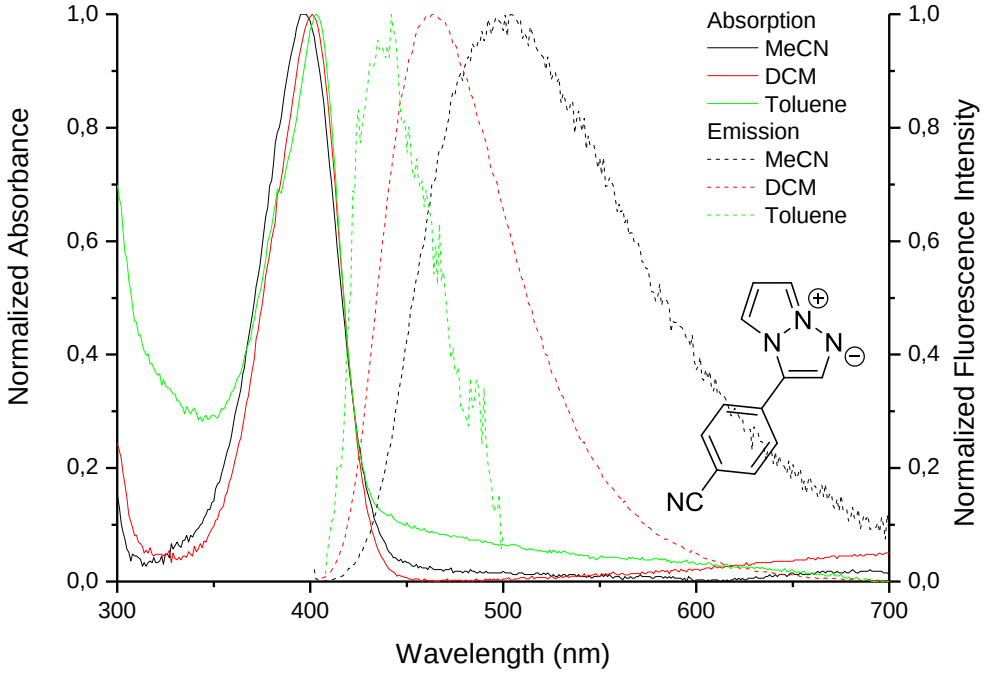


Figure S7. Normalized, visible absorption spectra of 3-(4-cyanophenyl)-1,3a,6a-triazapentalene **11d** in MeCN, DCM and toluene and the corresponding normalized fluorescence emission spectra.

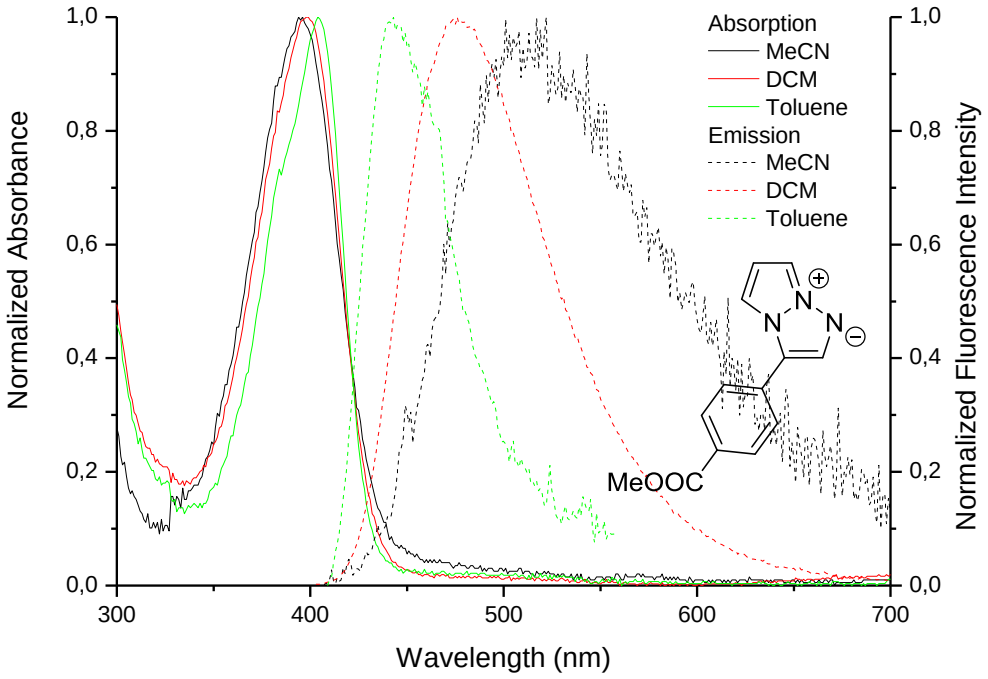


Figure S8. Normalized, visible absorption spectra of 3-(4-(methoxycarbonyl)phenyl)-1,3a,6a-triazapentalene **11e** in MeCN, DCM and toluene and the corresponding normalized fluorescence emission spectra.